ELSEVIER

Polymer 42 (2001) 6687–6697

polymer

www.elsevier.nl/locate/polymer

Comparative DSC kinetics of the reaction of DGEBA with aromatic diamines.

I. Non-isothermal kinetic study of the reaction of DGEBA with *m*-phenylene diamine

V.L. Zvetkov*

Central Laboratory of Physical Chemical Mechanics, Bulgarian Academy of Sciences, IV km, I bl., 1113 Sofia, Bulgaria

Received 20 August 2000; received in revised form 30 January 2001; accepted 23 February 2001

Abstract

The reaction kinetics of different epoxy–aromatic diamine systems is a of great importance in the processing of the so called high-technology composite materials. Since the epoxy–amine reaction is strongly exothermic, at moderate and high temperatures it proceeds in significant gradient. Therefore, the processing requires substantial knowledge of the reaction kinetics under programmed temperature conditions.

Differential scanning calorimetry (DSC) is the only direct reaction rate method which operates in two modes: constant temperature or linear programmed mode. This permits two kinds of kinetic analysis to be performed. The second technique is simply known as non-isothermal kinetics. Up to now, it is not sufficiently elucidated with regard to the epoxy–amine reaction although highly reproducible experimental data are possible to acquire.

The first part of the present study concerns the non-isothermal reaction kinetics of an epoxy resin based on diglycidyl ether of bis-phenol A (DGEBA) with *m*-phenylene diamine (mPDA). In order to obtain reliable data, we performed a mechanistic-like four stage kinetic analysis consisting of: (i) multiple curve methods involving different heating rates (also known as isoconversional or apparent kinetic methods); (ii) analysis at the peak maximum of the DSC curves; (iii) integral and differential single curve methods; and (iv) modeling of the reaction and comparison of the model with the experiment.

The apparent activation energy, $E_{ap} = 52.3\ \mathrm{kJ\ mol^{-1}}$, was calculated applying isoconversional methods. The analysis at the peak maximum temperatures of the DSC curves was carried out with the aid of E_{ap}. It validated the overall three molecular velocity equation of the reaction under programmed temperature regime rejecting other possible kinetic models – lower than three 'overall reaction order' autocatalytic and bimolecular non-catalytic ones. The velocity equation of the form: $d\alpha/dt = K_0 \exp(-E_a/RT)(B + \alpha)(1 - \alpha)^2$, was evaluated using single DSC curve methods, i.e. the activation energy, E_a, the pre-exponential factor, K_0, and the initial hydroxyl to epoxy ratio, B, were determined at different scanning rates. Modeling of the reaction in programmed temperature mode showed that reliable set of kinetic data, $E_a = 50.5\ \mathrm{kJ\ mol^{-1}}$, was obtained at heating rates below $5\ \mathrm{K\ min^{-1}}$.

The isoconversional methods indicated that side reaction at high degrees of conversion probably took place, whereas the single DSC curve kinetics exhibited non-typical false kinetic compensation effect above $5\ \mathrm{K\ min^{-1}}$. The modeling predicted incomplete curing at the end of the scanning experiments which was supposed to be one of the reasons for the latest findings.

As a result, this four stage kinetic analysis enabled us to ascertain the three molecular autocatalytic model of the reaction between DGEBA and mPDA, as well as to measure its overall kinetic parameters under programmed temperature conditions.

Keywords: Epoxy–amine reaction; Non-isothermal DSC; Autocatalytic kinetics

1. Introduction

The study of Horie et al. [1] was the first important investigation on the isothermal DSC kinetics of the epoxy–amine addition. Assuming three molecular hydroxyl complex in transition state, the third-order autocatalytic kinetics of this reaction, first proposed by Smith [2], was confirmed and methods for processing of experimental, mostly DSC data, were developed. The approach of Horie et al. is widely used for solving the inverse kinetic problem of different epoxy–amine reactions and even HPLC, FTIR,

---

* Tel.: +359-2-9793905; fax: +359-2-703433.
E-mail address: zvetval@bgcict.acad.bg (V.L. Zvetkov).

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00160-4

dielectric, and T_g-monitoring data are analyzed in a similar manner.

Although based on a certain mechanism, the approach of Horie et al. is not truly mechanistic, since a velocity equation having two (in some cases one) experimentally obtainable rate constants cannot exactly represent the kinetics of such a complex reaction as epoxy–amine addition [3–9]. The results show that the epoxy–amine kinetics satisfactorily obeys the model of Horie et al., when the speed of the main reaction is high compared to the speed of any side reaction. The activation energy, E_a, of the autocatalytic rate constant has been usually determined within the range of 45–60 kJ mol^{-1} for almost all epoxy–amine systems [10–21]. This important result has been obtained by many authors despite of the type of the amine component, the physical method (DSC under isothermal conditions, HPLC, FTIR, T_g-monitoring), and even of the form of the autocatalytic model [22–31]. Superposition of isothermal curves—degree of conversion versus log(time)—has also been used to fit the experimental data. The Arrhenius plot of the shift-factor yields an overall E_a within the mentioned limits.

In order to describe the complicated kinetics of the epoxy–amine reaction, attempts have been made to modify the model of Horie et al. applying empirical or semi-empirical velocity equations [22–31]. Recent investigations show that the deviations from the overall three molecular velocity equation of the epoxy–amine reactions are probably due to: (i) the different reactivity of the primary and secondary amine hydrogen atoms [3–5] usually in the presence of a side reaction [6,7] and (ii) the transfer of the rate determining step [8,9]. Some physical chemical processes or methodological factors [26,31] might also lead to deviations from the overall model of Horie et al.

The inverse kinetic problem of the epoxy–amine addition under programmed temperature regime has also been tested, but it has not yet been sufficiently cleared [13,32–41]. Using multiple DSC curve methods, the apparent E_a has been found to agree well with E_a of the isothermally determined autocatalytic constant [32–35,40]. Having in mind the main assumption of the isoconversional methods, namely, uniform mechanism up to a given degree of conversion, this result does not seem unexpected. On the contrary, serious disagreement between the isothermal and non-isothermal kinetics has been established when a single-curve method and a formal n-th order model [13,18,36–39] are applied. The apparent E_a, determined within the range of 80–110 kJ mol^{-1}, has been found to differ strongly from the E_a value obtained under isothermal conditions. Although different explanations of this fact have been discussed [13,36], inappropriate kinetic model function under non-isothermal conditions, namely formal n-th order or mechanistic-like second order model, is to be considered as one of the most probable reasons for the mentioned discrepancy.

The present study is focused on the non-isothermal DSC kinetics of an epoxy–amine reaction. Its aim is mechanistic-like solution of the inverse kinetic problem, i.e. validity test of the Horie et al. model, under programmed temperature conditions.

2. Background

The velocity equation of epoxy–amine reactions has been worked out in an absolute concentration form [1], but in almost all subsequent publications it has appeared in dimensionless form. The kinetics of equimolar formulations is represented with the following equation:

$$\frac{d\alpha}{dt} = (K' + K\alpha)(1-\alpha)^2 = K(B+\alpha)(1-\alpha)^2 \quad (1)$$

where: α is degree of conversion of the epoxy groups; K and K' are Arrhenius type rate constants which relate, respectively, to the autocatalytic and impurity catalytic (and/or non-catalytic) act of addition of an amine hydrogen atom to the epoxy ring; B is a dimensionless parameter which has different physical meaning depending on the reaction mechanism.

Eq. (1) is usually referred to as the Horie et al. overall velocity equation. It has been derived on the basis of the approximation that the reactivity of the primary and secondary amine hydrogen atoms is equal.

Other models, such as the well known from heterogeneous kinetics Prout–Tompkins type equation, have been also applied to describe the epoxy–amine addition kinetics. The last one has been proposed as a 'general' velocity differential equation of the reaction [22], viz.

$$\frac{d\alpha}{dt} = (K' + K\alpha^m)(1-\alpha)^n = K(B+\alpha^m)(1-\alpha)^n \quad (2)$$

where: restricting condition, $m + n = 2$ [22–24] or $m + n = 2.5$ [25], is usually introduced.

In terms of homogeneous kinetics, Eq. (2) is empirical since it does not take into account the stoichiometric ratio of the reaction components or the presence of side reactions. From a macrokinetic point of view, Eq. (2) has mechanistic-like (or more exactly semi-empirical) meaning in the following cases:

- $m = 0$ and $n = 1$ or $n = 2$, expressing non-catalytic rate determining step and resulting first [11,12] or second [13] order kinetics;
- $m = 1$ and $n = 2$, representing formation of an epoxy–amine–hydroxyl transition state complex [1];
- $m = 1$ and $n = 3/2$ or $n = 1$, describing lower order with respect to the amine component [26,27];
- $m = 3/2$ and $n = 2$, exhibiting competitive initiation mechanisms [8].

The cases $m = 1$ lead to another semi-empirical velocity equation [25–30] that directly relates to the present study. If the E_a values of the rate constants K and K' are equal, B is a temperature independent parameter and this model can be applied under programmed temperature regime, viz.

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} = K_0\exp(-E_a/RT)(B + \alpha)(1 - \alpha)^n \qquad (3)$$

where: dT/dt is the scanning rate.

Eq. (3) has analytical solution when: $n = 1/2, 1, 3/2$, and 2 (see Appendix A). Hence, different methods – isoconversional, differential and integral – might be applied investigating the non-isothermal kinetics. Numerical solution of the integral function $g(\alpha)$ is also available [42].

The non-isothermal kinetics of the epoxy–amine reaction based on autocatalytic model is, surprisingly, considered in only one publication [41]. The isothermal kinetics of the same system has shown that B is a temperature independent parameter [16]. More often, K' and K have different E_a, but either the difference between E'_a and E_a is negligible or K' is at least two orders of magnitude less than K in a wide temperature range. Therefore, it is correct to assume that $B = \text{const}$. This approximation might lead to some increase of E_a of the autocatalytic constant, but it is an essential compromise when the non-isothermal kinetics of the epoxy–amine reaction is being studied.

3. Experimental

3.1. Sample preparation

The epoxy resin used in this study was highly purified low molecular homologue of DGEBA, under the trade name DER-332 of Dow Chemical, supplied by Fluka. Its epoxy equivalent, measured by different methods [43], was 174 kg kmol^{-1}. mPDA, 99% purity grade and also provided by Fluka, was applied as aromatic diamine hardener. Stoichiometric amounts of the two components were melted at 70°C (343 K) and undercooled at 55°C (328 K). The monomers were mixed in a high speed stirrer for 10 min at this temperature and 10 min during the cooling to room temperature. After degassing under vacuum, small amounts of the reactive mixture (approximately 12–15 mg) were poured into aluminum capsules. The samples were placed in plastic bags and, inside in a desiccator, kept in a refrigerator at −20°C (253 K). Before each experiment, the samples were removed from the refrigerator and allowed to reach thermal equilibrium with the environment into the bags for at least 15–20 min [16].

3.2. Experimental technique

The experimental method used in this study was the differential scanning calorimetry. A Perkin Elmer DSC-2C instrument, interfaced to 3600 Data Station with appropriate data acquisition and analytical software, was applied as experimental technique. At the beginning of the investigation, the test points of the instrument were measured and, if necessary, adjusted to their factory settings. Thus, excellent signal to noise ratio was attained. The calibration was regularly made using In and Zn standards at each scanning rate being used. Special attention to the slope of the baseline was paid controlling the Y-value at the final temperature, T_f. (At the end of each experiment the $(dH/dt)_f$ value was kept constant.) The first heating was performed at $dT/dt = 10$, 5, and 2.5 K min^{-1} in a temperature interval from 223 K to the corresponding T_f. The second scans were recorded at 10 K min^{-1} from 253 to 473 K after cooling the reacted samples from T_f to 253 K at 80 K min^{-1}. Using at least three data files, the integral parameters, which characterize the reaction of DGEBA with mPDA under programmed temperature conditions, were determined.

The initial reaction temperature, T_i, was assumed as the temperature 10 K less than the one, at which significant deviation from the baseline, $dH/dT = 0.00005$ kJ kg^{-1} K^{-1}, was observed. T_f was defined as the upper limit of the 10 K temperature range, where the slope of the baseline was the same as that at the beginning of the reaction, viz.: $\Delta(dH/dT)_f/\Delta T = \Delta(dH/dT)_i/\Delta T$. The reproducibility of T_i and T_f values was within ±5 K.

The reaction enthalpy, ΔH_0, the temperature at the maximum of the DSC curves, T_p, the onset glass transition temperature and the jump of the isobaric specific heat capacity of the monomer mixture, T_{g0} and ΔC_{p0}, were measured from the first DSC scans. The corresponding glass transition parameters of the reacted specimens, T_{gf} and ΔC_{pf}, were measured from the second DSC curves after cooling the samples from T_f to 253 K at 80 K min^{-1} and subsequent scanning at 10 K min^{-1}.

The change of the specific heat capacity during the reaction, ΔC_{pt}, was determined in the following manner. It is experimentally established that dC_{pf}/dT above T_{gf} and dC_{p0}/dT above T_{g0} are approximately equal [43]. Therefore, ΔC_{pt} is the difference between C_{pf} and C_{p0}, extrapolated at a reference temperature, viz. $\Delta C_{pt} = (C_{pf} - C_{p0})_T$. On the other hand, ΔC_{pt} is defined as deflection from the baseline, $\Delta C_{pt} = [(dH/dT)_f - (dH/dT)_i]_T$, since $\Delta(dH/dT)_f/\Delta T = \Delta(dH/dT)_i/\Delta T$ is an initial experimental condition. The current value of the specific heat capacity, C_{pc}, is iteratively calculated based on the assumption that C_{pc} is proportional to α. Thus, ΔC_{pt} is used as a methodological correction of the baseline during the reaction.

Applying the above described experimental procedures, the reproducibility of the data was within the specified by Perkin Elmer values, independent of the heating rates being used: ±8 kJ kg^{-1} (for ΔH_0); ±0.3 K (for T_p); ±0.005 kJ kg^{-1} K^{-1} (for ΔC_p); ±0.5 K (for T_{g0}); and ±1 K (for T_{gf}).

3.3. Analytical methods

The original experimental data were collected in a Perkin Elmer 3600 Data station, coupled to the DSC instrument through the standard or specific heat data acquisition software. Then, the data files were transferred in a personal computer (DX2-486, DOS 6.2). Further kinetic analysis was performed with the aid of a self developed software, written in C++ programming language. It is structured in two main modules—Curve fitting and Modeling—so either the inverse or direct kinetic problem can be solved.

In the present version of the program, both the simulating and fitting procedures are based on the following biconstant kinetic model:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} = K_0 \exp(-E_a/RT)(B + \alpha^m)(1-\alpha)^p \times (R_0 - \alpha)^q \quad (4)$$

where: m, p, and q are power exponents, their sum being restricted to 3; R_0 is ratio of the components (in particular, the initial amine to epoxy ratio).

In the curve fitting section, B is a temperature independent parameter, i.e. an apparent E_a is being determined. In the modeling section, B is a relation of two rate constants K' and K, which might have different E_a values. Changing the power exponents of Eq. (4), the macrokinetics of a large number of chemical reactions, either formal or mechanistic-like, can be described.

4. Results and discussions

4.1. Apparent reaction parameters

The non-isothermal curves, $d\alpha/dT$ versus T, of the polyaddition reaction of DGEBA and mPDA obtained at $dT/dt = 10$, 5, and 2.5 K min^{-1} are shown in Fig. 1. Each curve averages three data files. The integral reaction parameters are summarized in Table 1.

The data in Table 1 are statistical results of at least three values of the corresponding parameter. Although within the error limits, ΔH_0, T_{g0} and ΔC_{g0} seem to be linear functions of dT/dt. While the dependence of ΔH_0 on dT/dt is supposed to have chemical nature, the dependencies of T_{g0} and ΔC_{p0} on dT/dt are more probably methodological.

The molar enthalpy of the reaction of DGEBA with mPDA at $dT/dt = 5$ K min^{-1}, $\Delta H^0 = 110$ kJ mol^{-1}, is close to that obtained by other authors [10]. The extrapolated at zero heating rate ΔH^0 value is one of the highest found in literature. Since T_g values of the fully and partially reacted compositions were measured at $dT/dt = 10$ K min^{-1}, $\Delta T_g = -4.5$ K is the onset T_g correction at $dT/dt = 0$, i.e. under isothermal conditions. On the other hand, the ΔC_{pt} value is used as a methodological correction of the baseline during the reaction applying the above described iteration mathematical procedure.

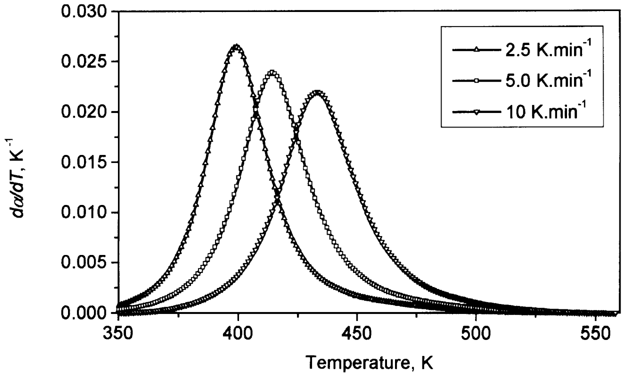

Fig. 1. $d\alpha/dT$ versus temperature plot of the reaction of DGEBA with mPDA at different dT/dt.

Our investigation concept concerning the non-isothermal reaction kinetics of DGEBA with aromatic diamines consists of four subsequent steps discussed in separate subsections.

4.2. Kinetic analysis of the DSC data obtained at different heating rates

The multiple curve variable plots, $d\alpha/dt$ versus T and α versus T, of the reaction of DGEBA with mPDA are presented in Figs. 2 and 3, respectively.

The differential isoconversional method of Friedmann [44] obeys the expression:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\frac{d\alpha}{dT}\frac{dT}{dt}\right) = \ln[f(\alpha)] + \ln K_0 - \frac{E_a}{RT} \quad (5)$$

The multiple curve method of Ozawa [45] is a rearrangement of the Doyle's temperature integral solution [46] into the following equation:

$$\log(dT/dt) = \log\left(\frac{K_0 E_a}{R}\right) - \log[g(\alpha)] - c - l\frac{E_a}{RT} \quad (6)$$

where: c and l are couple tabulated coefficients.

The main problem of the Ozawa method consists in the accurate setting of the coefficients c and l. The most frequently

Table 1
Integral parameters of the reaction of DGEBA with mPDA

dT/dt (K min^{-1})	ΔH_0 (kJ kg^{-1})	T_{g0} (K)	ΔC_{p0} (kJ kg^{-1} K^{-1})	ΔC_{pt} (kJ kg^{-1} K^{-1})	T_{gf}[a] (K)	ΔC_{pf}[a] (kJ kg^{-1} K^{-1})	T_i (K)	T_f (K)	T_p (K)
10	536	252.5	0.605	0.315	431	0.355	343	568	432.9
5	547	250.0	0.610	0.315	433	0.355	328	553	414.7
2.5	553	249.0	0.615	0.315	436	0.350	313	538	398.6
0[b]	558	248.0	0.620	0.315					

[a] After second scanning at $dT/dt = 10$ K min^{-1}.

[b] Linear extrapolation at $dT/dt = 0$.

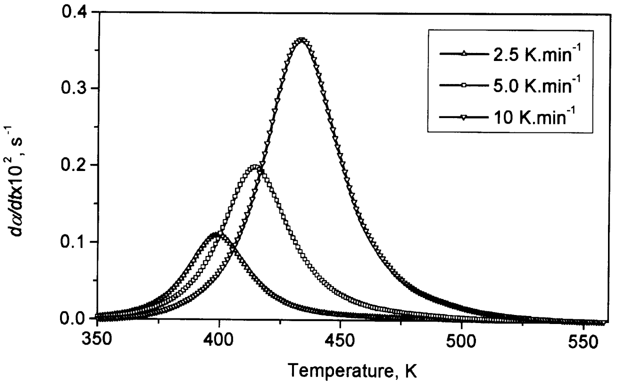

Fig. 2. $d\alpha/dt$ versus temperature plot of the reaction of DGEBA with mPDA at different dT/dt.

used values are: $c = 2.313$ and $l = 0.4567$ if $E_a/RT = 28–50$, or $c = 2.000$ and $l = 0.4667$ if $E_a/RT = 18–30$ [47,48]. The analysis of the reaction of DGEBA with aromatic diamines shows that the relation $E_a/RT = 13–20$ is significantly less and the values of the coefficients c and l differ from the universal ones, viz. $c = 1.600$ and $l = 0.4880$.

As is well known, a uniform mechanism up to a given degree of conversion is the fundamental assumption of the isoconversional methods. This means that the concentration function $f(\alpha)$ in Eq. (5), or its integral solution $g(\alpha)$ in Eq. (6), do not depend on the scanning rate at a fixed value of the variable α. The plot of $\ln(d\alpha/dt)$ versus $1/T$ and that of $\log(dT/dt)$ versus $1/T$ yield the apparent activation energy, even if the analytical expression of the velocity equation is unknown.

Fig. 4 shows the plot of E_a versus α. The mean E_{ap} values obtained using the methods of Friedmann and Ozawa and their standard deviations are given in Table 2. The results graphically represented in Fig. 4 and summarized in Table 2 might be explained as follows.

The data scattering of the Ozawa method is less than that of the Friedmann method. This result is quite logical since the input variables of the Friedmann method are three, while the Ozawa method is a two-variable one.

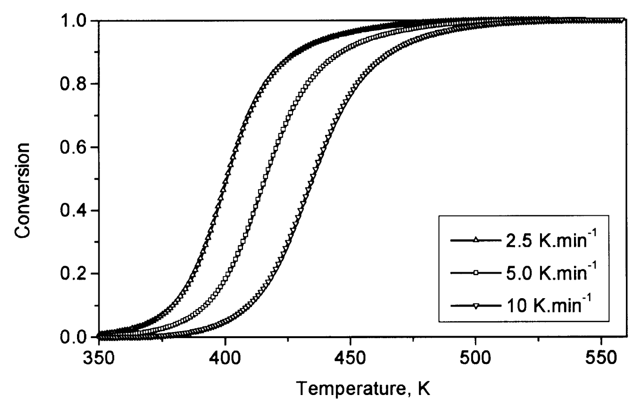

Fig. 3. Degree of conversion of the epoxy groups versus temperature plot at different dT/dt.

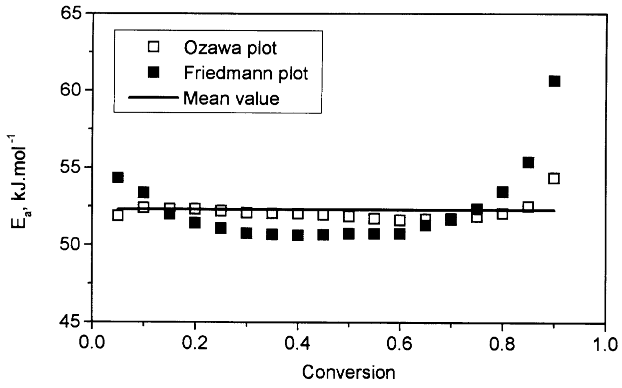

Fig. 4. Dependence of the activation energy on the degree of conversion according to the Ozawa and Friedmann methods.

The change of the baseline during the reaction does not affect either the character of the dependence of E_a on α or the mean E_{ap} value. Having in mind this estimate, baseline corrected experimental data are further analyzed.

The mean E_{ap} values of the two methods are close to each other. Therefore, the values of the Doyle's coefficients c and l, proposed by us, seem to be correct. The universal value of l, viz. $l = 0.4567$, leads to an increase of E_{ap} by approximately 8%.

The dependencies of E_a on α, according to the methods of Friedmann and Ozawa, differ slightly only within the range of $\alpha = 0.05–0.15$. Both methods show that a side reaction probably takes place at high temperatures and degrees of conversion since E_a increases at the end of the reaction, $\alpha = 0.75–0.90$.

The results in Table 2 correlate with those obtained by other authors investigating DGEBA–aromatic diamine reactions with the aid of isoconvertional techniques [32–35,40]. The aim of these studies consists in predicting isothermal curves from dynamic DSC experiments without any assumption being made about the form of the velocity equation or reaction mechanism [33].

Our further analysis is based on the activation energy of the reaction and requires the expression of the velocity equation. As the results in Table 2 show, the presence of a side reaction does not significantly alter the mean E_{ap} value in contrast to E_a measured using single DSC curve methods above 5 K min^{-1}. This fact will be discussed later in more detail.

4.3. Kinetic analysis at peak maximum temperature

From a purely mathematical point of view, the second derivative of α against T at the maximum of the DSC curve becomes zero, viz.

$$\frac{d^2\alpha}{dT^2} = K_0\exp\left(-\frac{E_a}{RT_p}\right)\left\{\frac{E_a}{RT_p^2}f(\alpha_p) + \frac{d[f(\alpha_p)]}{dT}\right\} = 0 \quad (7)$$

Table 2
Apparent activation energy, obtained using isoconvertional methods

Method	Original curves				Baseline corrected curves			
	$\alpha = 0.15$–0.75		$\alpha = 0.05$–0.90		$\alpha = 0.15$–0.75		$\alpha = 0.05$–0.90	
	E_{ap} (kJ mol^{-1})	SD (kJ mol^{-1})	E_{ap} (kJ mol^{-1})	SD (kJ mol^{-1})	E_{ap} (kJ mol^{-1})	SD (kJ mol^{-1})	E_{ap} (kJ mol^{-1})	SD (kJ mol^{-1})
Friedmann	51.10	0.6	52.30	2.7	51.15	0.6	52.35	2.5
Ozawa	51.95	0.3	52.10	0.7	52.00	0.25	52.20	0.6

Assumption of the model, expressed by Eq. (3), leads to:

$$\frac{E_a}{RT_p^2}(B+\alpha_p)(1-\alpha_p)^n + \left(\frac{d\alpha}{dT}\right)_p [(1-\alpha_p)^n - n(B+\alpha_p) \times (1-\alpha_p)^{n-1}] = 0$$

Rearranging the above equation against the parameter B, one can obtain:

$$B = \frac{1}{\frac{n}{1-\alpha_p} - \frac{E_a}{RT_p^2} \Big/ \left(\frac{d\alpha}{dT}\right)_p} - \alpha_p \qquad (8)$$

T_p, $(d\alpha/dT)_p$, and α_p are important characteristics in the non-isothermal kinetics. If the form of $f(\alpha)$ and $g(\alpha)$ is known, E_a can be calculated. On the contrary, if E_a is previously determined, the validity of a given kinetic model can be estimated.

The second approach is applied in this study. An attempt is made to ascertain the autocatalytic model of the reaction of DGEBA with mPDA assuming: (i) the values of T_p, $(d\alpha/dT)_p$, and α_p experimentally measured; and (ii) $E_a = 52.3$ kJ mol^{-1} determined using isoconversional methods.

The analysis at T_p of the partially reacted DGEBA–mPDA samples is also a convenient way to test the kinetic model. An expression of the parameter B can be easily derived based on the energy balance, viz. $B = B'(1-\alpha_0) - \alpha_0$ (see Appendix B).

The parameters at T_p and the calculated values of B at $dT/dt = 10$, 5, and 2.5 K min^{-1} of the unreacted samples and those of the partially reacted samples measured at $dT/dt = 10$ K min^{-1} are given in Table 3.

The data show that the kinetic model of Horie et al., or $n = 2$, satisfactorily describes the relationship at T_p although the value of B is somehow less than the expected one ($B > 0.015$ for the epoxy resin being used [15]). This estimate is most probably due to the fact that the mathematical condition $d^2\alpha/dT^2 = 0$ at T_p is under consideration from a methodological point of view [49,50]. The test of the velocity equation when $n < 2$ fails. As one can establish, the values of B are extremely high if $n = 3/2$.

Unreliable reaction order is also found assuming a formal n-th order model, i.e. $n = 0.828$. Conversely, the use of a second order non-catalytic velocity equation leads to a rather high E_a value, $E_a = 126$ kJ mol^{-1}. It exceeds more than two times E_{ap} obtained using isoconversional methods. On the other hand, many authors measured E_a within 80–110 kJ mol^{-1} [13,18,36–39] based on formal n-th order model (in particular, $n = 2$, or non-catalytic bimolecular mechanism of the epoxy–amine reaction). Our analysis shows that transfer of the rate determining step, and resulting second order kinetics under programmed temperature regime [13], seems to be inconsistent with the aforementioned results.

Therefore, the autocatalytic three molecular velocity equation of the reaction between DGEBA and mPDA seems to be operative under programmed temperature conditions since other possible kinetic models—lower than three 'overall reaction order' autocatalytic and bimolecular non-catalytic ones—have been rejected.

4.4. Kinetic analysis using single DSC curve methods

The following single curve kinetic methods under programmed temperature conditions are applied in the present study:

- method I – iterative integral curve approximation method;
- method II – the best differential fit of the velocity equation;

Table 3
Peak maximum characteristics of DGEBA–mPDA compositions at different dT/dt and initial degree of conversion. $E_{ap} = 52.3$ kJ mol^{-1}

dT/dt (K min^{-1})	α_0	T_p (K)	$(d\alpha/dT)_p$ (K^{-1})	α_p	$E_{ap}/RT_p^2(d\alpha/dT)_p$	B ($n = 2$)	B ($n = 3/2$)
10	0	432.9	0.02195	0.4590	1.529	0.002	0.345
5.0	0	414.7	0.02390	0.4565	1.530	0.009	0.357
2.5	0	398.6	0.02640	0.4530	1.500	0.011	0.352
10	0.06	427.4	0.0182	0.467	1.893	0.004	0.521
10	0.09	425.3	0.0168	0.474	2.070	0.006	0.643
10	0.12	424.8	0.0159	0.476	2.192	0.003	0.778

- method III – integral method of the form of Coats and Redfern [51].

Method I is based on a purely numerical trial and error algorithm. If the form of the velocity equation is known, some of the reaction parameters, e.g. R_0 and n, have to be entered. Then, the simulated integral curve is compared to the experimental one 'shooting' the remaining parameters. This procedure is repeated until the best fit between the simulated and experimental curve is achieved. Finally, the program outputs the unknown kinetic parameters, E_a, K_0, and B. Four parameter fitting procedure is somewhat speculative although it also predicts that $n \approx 2$. The third order velocity equation has analytical solution, see Eq. (11), and a test of the algorithm at $dT/dt = 2.5\ \mathrm{K\ min^{-1}}$ has shown excellent correlation between method I and the well-known method of Doyle [46,47].

Method II approximates the experimental data to the logarithmic form of Eq. (3), viz.

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln K_0 - \frac{E_a}{RT} + \ln(B+\alpha) + n\ln(1-\alpha) \qquad (9)$$

where: E_a, K_0, and B are measured using non-linear regression; and $n = 2$.

The differential methods, such as that of Borchardt and Daniels [49], are simply applied to formal n-th order reactions. As is shown later, it well describes other chemical reactions which are controlled by a significant rate constant.

Method III is based on the following approximate solution [51]:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{K_0 R}{E_a dT/dt}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \qquad (10)$$

The analytical expressions of $g(\alpha)$ for different values of n are derived in Appendix A. If $n = 2$, then:

$$g(\alpha) = \frac{1}{1+B}\frac{\alpha}{1-\alpha} + \frac{1}{(1+B)^2}\ln\frac{B+\alpha}{B(1-\alpha)} \qquad (11)$$

The kinetic parameters of the reaction of DGEBA with mPDA determined with the aid of single curve DSC methods are presented in Table 4. The analysis of the results in Table 4 shows the following trends:

- all kinetic parameters measured at $10\ \mathrm{K\ min^{-1}}$ are strongly affected by the kinetic method being applied;
- the values of E_a and K_0 determined at lower heating rates are slightly influenced by the kinetic method, in contrast to the parameter B; moreover, the E_a value measured at $2.5\ \mathrm{K\ min^{-1}}$ is comparable to that obtained using isoconversional methods;
- both E_a and K_0 are strongly increasing functions of dT/dt and the plot of E_a versus $\ln(K_0)$ is approximately linear independent of the kinetic method.

In the non-isothermal kinetics of heterogeneous reactions [48] the linear relationship between E_a and $\ln(K_0)$ is known as the kinetic compensation effect. If the dependencies, E_a versus dT/dt and E_a versus α, change in the same direction this effect is real, otherwise, it is usually a result of an inappropriate kinetic model. Both the constancy of the isoconversional dependence of E_a versus α in a large temperature interval and the analysis at T_p have rejected the last possibility, i.e. the model of Horie et al. has been proved to be valid.

Then, the false kinetic compensation effect of the reaction of DGEBA with mPDA might be related to the form of the autocatalytic function. Its mathematical analysis shows that the parameter B affects the values of $f(\alpha)$ and $g(\alpha)$ at the beginning rather than at the end of the reaction. Hence, if the slope of the plot of $\ln[(d\alpha/dt)/f(\alpha)]$ versus $1/T$ (or the relation E_a/R) increases at high degrees of conversion, its initial part is easily adjusted to a straight line by an increase of the parameter B. Therefore, an important suggestion can be drawn from the results represented here: the non-isothermal kinetics of the reaction of DGEBA with aromatic amines is preferable to investigate at relatively low heating rates, $dT/dt < 5\ \mathrm{K\ min^{-1}}$.

The kinetic data, presented in Table 4, seem to confirm the above suggestion. The E_a value obtained at $dT/dt = 2.5\ \mathrm{K\ min^{-1}}$, $E_a = 50.5\ \mathrm{kJ\ mol^{-1}}$, is comparable to E_{ap} determined using isoconversional methods. On the other side, a single DSC curve test performed at $dT/dt = 1.25\ \mathrm{K\ min^{-1}}$ also yields $E_a = 50$–$51.5\ \mathrm{kJ\ mol^{-1}}$ depending of the method.

4.5. Comparison of computer simulated data with experimental data

The solution of the direct kinetic problem is the best way to test the accuracy of the kinetic parameters. For this purpose, numerical modeling of the reaction under

Table 4
Apparent kinetic parameters of the reaction of DGEBA–mPDA compositions, obtained using single DSC curve methods at different dT/dt

Method	Kinetic parameters								
	$dT/dt = 2.5\ \mathrm{K\ min^{-1}}$			$dT/dt = 5\ \mathrm{K\ min^{-1}}$			$dT/dt = 10\ \mathrm{K\ min^{-1}}$		
	E_a (kJ mol^{-1})	log K_0 (s^{-1})	B	E_a (kJ mol^{-1})	log K_0 (s^{-1})	B	E_a (kJ mol^{-1})	log K_0 (s^{-1})	B
Method I	50.5	4.47	.0300	56.9	5.26	.0558	69.00	6.67	0.1032
Method II	51.64	4.66	.0218	55.6	5.13	.0438	65.31	6.23	0.0922
Method III	52.55	–	.0284	54.6	–	.0389	60.00	–	0.0526

Table 5
Peak maximum parameters of the computer simulated curves of the reaction of DGEBA with mPDA under programmed temperature conditions at different dT/dt

Kinetic parameters			dT/dt (K min^{-1})	Peak maximum characteristics		
E_a (kJ mol^{-1})	K_0 (s^{-1})	B		T$_p$, (K)	$(d\alpha/dT)_p$ (K^{-1})	α_p
69.0	4.72×10^6	0.103	10	432.9	0.02145	0.4760
			5.0	419.2	0.02285	0.4765
			2.5	406.2	0.02430	0.4765
50.5	2.98×10^4	0.030	10	433.1	0.02125	0.4500
			5.0	415.1	0.02315	0.4500
			2.5	398.6	0.02525	0.4495

programmed temperature conditions is incorporated in our self developed software. An optimized algorithm of the well-known fourth/fifth order Runge–Kutta method is applied. Special attention to T_i is kept. It is defined as the temperature up to which the degree of conversion in 50 K interval vanishes zero, $\alpha_0 < 0.00005$. Thus, the accumulative error is minimized and the data at T_p of the simulated curves are highly reproducible.

Numerical modeling of the reaction of DGEBA with mPDA is performed at dT/dt = 10, 5, and 2.5 K min^{-1}. The experimental values of T_p, $(d\alpha/dT)_p$, and α_p are test characteristics of the numerical analysis. The modeling parameters have been obtained in the previous subsection using method I at two heating rates – 10 and 2.5 K min^{-1}. The results of the performed investigation are represented in Table 5.

If the kinetic parameters are determined at dT/dt = 10 K min^{-1} the data in Table 5 show the following trends:

- T_p and $(d\alpha/dT)_p$ of the simulated curves satisfactorily correspond to the experimental values at 10 K min^{-1} only; serious disagreement between the modeling and the experiment at lower heating rates exists;
- the α_p values of the simulated curves, including at 10 K min^{-1}, significantly exceed the experimental ones;

If the modeling parameters are determined at dT/dt = 2.5 K min^{-1}, the data in Table 5 imply better correlation between the modeling and the experiment:

- the differences between the T_p values of the simulated and experimental curves are within the error limits at each heating rate;
- α_p of the simulated curves is nearly the same as the experimental value;
- the differences between the simulated and experimental α_p and $(d\alpha/dT)_p$ values are small enough to ascertain the kinetic model; the first one is a slightly increasing function of dT/dt which is a logical finding having in mind the DSC principle [49,50].

The kinetic data obtained using the best simultaneous differential curve modeling, and assuming $E_a = 50.5$ kJ mol^{-1}, are shown in Table 6.

The excellent correlation between the modeling and the experiment with respect to T_p and $(d\alpha/dT)_p$ implies that the E_a value determined at dT/dt = 2.5 K min^{-1} seems to be correct. The higher α_p values can be attributed to the above mentioned methodological factors [49,50]. Clearly, the disadvantages of the single DSC curve kinetics have been compensated by the reaction modeling.

4.6. General remarks

As one can establish, neither isoconversional nor single DSC curve kinetics provides sufficient and reliable data that are possible to obtain by using a four stage non-isothermal approach. Each subsequent stage increases the significance of the kinetic data based on the results obtained in the preceding one. The results concerning the kinetics of the DGEBA–mPDA reaction can be summarized, as follows.

1. The apparent activation energy has been determined applying the most commonly used multiple DSC curve methods, namely $E_{ap} = 52.3$ kJ mol^{-1}. The isoconversional kinetics

Table 6
Comparison between the theory and experiment of the reaction of DGEBA with mPDA under programmed temperature conditions. $E_a = 50.5$ kJ mol^{-1}, $K_0 = 3.13 \times 10^4$ s^{-1}, $B = 0.025$

dT/dt (K min^{-1})	Experimental curves			Computer simulated curves		
	T_p, (K)	$(d\alpha/dT)_p$ (K^{-1})	α_p	T_p, (K)	$(d\alpha/dT)_p$ (K^{-1})	α_p
10	432.9	0.02195	0.4590	432.9	0.02205	0.4470
5.0	414.7	0.02390	0.4565	414.9	0.02405	0.4470
2.5	398.6	0.02640	0.4530	398.5	0.02625	0.4470

has also indicated that side reaction at high degrees of conversion probably proceeds.

2. The analysis at the peak maximum temperatures of the DSC curves has been carried out with the aid of E_{ap}. It has been shown that the three molecular velocity equation of the reaction under programmed temperature conditions seems to be valid. Other possible models, i.e. lower than three 'overall reaction order' autocatalytic and bimolecular non-catalytic ones, have been rejected.
3. The velocity equation has been evaluated using single DSC curve methods, i.e. a set of kinetic parameters has been determined at each scanning rate being used. Non-typical false kinetic compensation effect has been observed above 5 K min^{-1}. It has been found to disappear below this value.
4. The modeling of the reaction under programmed temperature regime has also shown that reliable kinetic parameters are obtained at scanning rates less than 5 K min^{-1}.

The results derived in the last two subsections enable us to evaluate the velocity equation of the DGEBA–mPDA reaction under programmed temperature conditions within the following limits:

$$\frac{da}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} = 2.98 \times 10^4 \exp(-50.5\ \text{kJ mol}^{-1}/RT) \times (0.030 + \alpha)(1-\alpha)^2\ \text{s}^{-1} \quad (12)$$

and:

$$\frac{da}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} = 3.13 \times 10^4 \exp(-50.5\ \text{kJ mol}^{-1}/RT) \times (0.025 + \alpha)(1-\alpha)^2\ \text{s}^{-1} \quad (13)$$

Having in mind that Eqs. (12) and (13) describe well the shift of the peak maximum temperature versus scanning rate, the above value of the activation energy is supposed to be reasonable.

Fig. 5 shows numerical test of the reaction kinetics of DGEBA with mPDA in a wide temperature range. Similar scheme as the one performed in the preceding subsection is accepted: modeling of the reaction at 10 K min^{-1} applying the kinetic parameters measured at 2.5 K $^{-1}$, and vice versa. The kinetic data measured at higher heating rate give unreliable results (Fig. 5a). The kinetic data obtained at lower heating rate seem to provide good correlation between the model and the experiment (Fig. 5b). Some deviations exist at relatively high degrees of conversion. The most probable reasons for this finding are:

- incomplete curing and/or topological restrictions at the onset of the process of destruction of the polymer;
- side reactions occurring together with the epoxy–amine addition;

However, in any case E_a of the second reaction is higher than that of the autocatalytic one. The lower scanning rates reduce the effect of the side reaction, but the possibility that the epoxy–amine reaction might become diffusion controlled should be also taken into account [40].

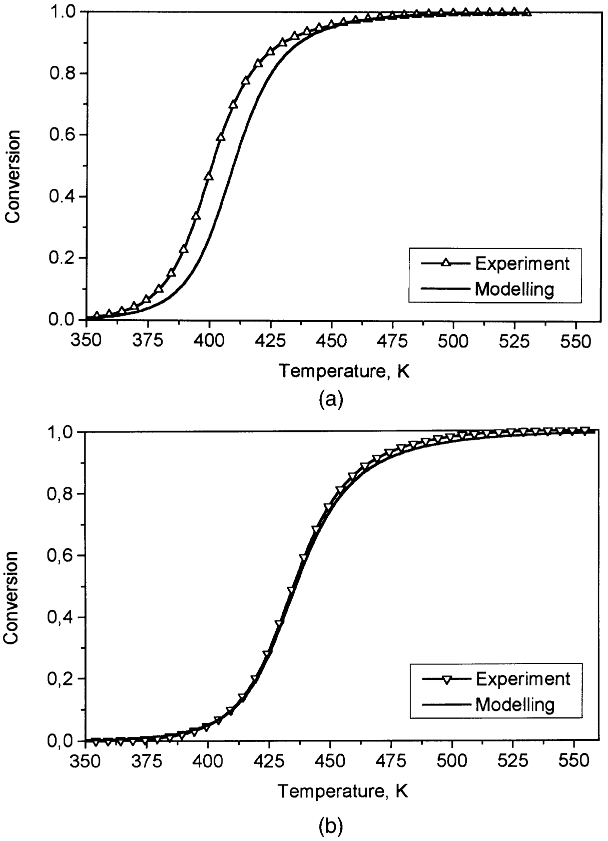

Fig. 5. Comparison between the theory and experiment of the reaction of DGEBA with mPDA under different conditions: (a) $dT/dt = 2.5$ K min^{-1}, $E_a = 69.0$ kJ mol^{-1}, $K_0 = 4.72 \times 10^6$ s^{-1}, $B = 0.103$; (b) $dT/dt = 10$ K min^{-1}, $E_a = 50.5$ kJ mol^{-1}, $K_0 = 2.98 \times 10^4$ s^{-1}, $B = 0.030$ (see the text).

The decreasing dependencies of ΔH_0 on dT/dt and, especially, of T_{gf} on dT/dt (see Fig. 6) are also convincing evidence that the deviations at high degree of conversion have most probably kinetic nature. Modeling of low activation energy reactions, such as the epoxy–amine addition, indicate that incomplete curing at experimentally measured T_f seems to be the case.

In order to test this possibility comparison between the model prediction of α_f at T_f and T_{gf} predicted α_f values, measured at different heating rates, has been performed. The second α_f data have been determined using the well-known DiBenedetto formula [52]. The results show that both the modeling and the T_g versus α dependence predict approximately equal values at the same heating rate: $\alpha_f = 0.999$ (at $dT/dt = 2.5$ K min^{-1}); $\alpha_f = 0.996$ (at $dT/dt = 5$ K min^{-1}); and $\alpha_f = 0.991$ (at $dT/dt = 10$ K min^{-1}).

Correcting the original data against the α_f value and repeating the single DSC curve kinetics and non-isothermal modeling leads to a sharp decrease of the difference between the lowest and highest E_a values, namely: 8 kJ mol^{-1}.

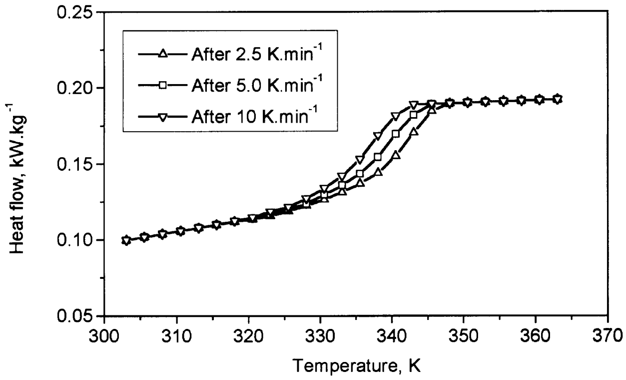

Fig. 6. Second scans of DGEBA–mPDA samples reacted at different dT/dt.

Better fit between the model and the experiment is achieved, as well.

5. Conclusions

The four stage kinetic approach, applied by us, has shown that the autocatalytic model of Horie et al. describes well the non-isothermal kinetics of the DGEBA–mPDA reaction, especially at low heating rates.

The velocity equation has been evaluated in programmed temperature mode with the aid of a single rate constant kinetic analysis. The value of its activation energy is comparable to the apparent activation energy calculated using isoconversional methods. This fact implies that the autocatalytic three molecular mechanism of this reaction predominates under programmed temperature regime up to relatively high degrees of conversion. It cannot be considered that this problem is sufficiently cleared in the literature.

Several observations have indicated that a side reaction at high degrees of conversion is probably taking place. These are: (i) the decreasing dependencies of the glass transition temperature of the reacted samples and the reaction enthalpy on the scanning rate; (ii) the false kinetic compensation effect at high heating rates; (iii) the increasing isoconversional dependence of the activation energy on the degree of conversion at high temperatures; and (iv) the modeling of the reaction under programmed temperature conditions.

The effect of the side reaction is reduced at low heating rates, but the possibility that the main reaction might become diffusion controlled should be also taken into account.

We have to point out that the derivation of an evaluated autocatalytic velocity equation of the DGEBA–mPDA reaction from dynamic DSC experiments is an approximation since the parameter B is assumed to be a constant. It is more often not a true. The epoxy–amine reactions are simply represented by a set of ordinary differential equations. However, if the three molecular autocatalytic model is supposed to be valid, the modeling of the reaction allows to perform a test of different reaction schemes in programmed temperature mode comparing the simulated non-isothermal data with the experiment.

Acknowledgements

The financial support of the National Fund ‘Scientific Investigation’ of the Bulgarian Ministry of Education and Science (Contracts X-209/1992 and X-538/1995) is gratefully acknowledged.

Appendix A. Analytical solution of the velocity differential equations.

The analytical solution of Eq. (5) when $m = 1$, and $n = 1$ or $n = 2$ is known [42], but since it directly refers to the present study its derivation is given below.

I. If $n = 2$, separating of the variables in Eq. (4) leads to:

$$\int_{\alpha_0}^{\alpha} \frac{\mathrm{d}\alpha}{(B+\alpha)(1-\alpha)^2} = \int_0^t K\mathrm{d}t \tag{A1}$$

The left hand side infinite integral has the following solution:

$$\int_{\alpha} \frac{\mathrm{d}\alpha}{(B+\alpha)(1-\alpha)^2} = \frac{1}{1+B}\frac{1}{1-\alpha} + \frac{1}{(1+B)^2}\ln\frac{B+\alpha}{1-\alpha} \tag{A2}$$

since:

$$\frac{1}{(B+\alpha)(1-\alpha)^2} = \frac{1}{1+B}\frac{1}{(1-\alpha)^2} + \frac{1}{(1+B)^2}\left(\frac{1}{B+\alpha} + \frac{1}{1-\alpha}\right)$$

Integrating Eq. (A2) from $\alpha_0 = 0$ to α gives:

$$\frac{1}{1+B}\frac{\alpha}{1-\alpha} + \frac{1}{(1+B)^2}\ln\frac{B+\alpha}{B(1-a)} = Kt \tag{A3}$$

II. If $n = 3/2$, the separating of the variables rearranges Eq. (6) to:

$$\int_{\alpha_0}^{\alpha} \frac{\mathrm{d}\alpha}{(B+\alpha)(1-\alpha)^{3/2}} = \int_0^t K\mathrm{d}t$$

In order to solve the above equation, it is necessary to put: $\alpha = 1 - \beta^2$; $\mathrm{d}\alpha = -2\beta\mathrm{d}\beta$; and($b^2 = B + 1$. Thus, the equation below is obtained:

$$-2\int_{\beta_0}^{\beta} \frac{\mathrm{d}\beta}{(b^2-\beta^2)\beta^2} = \int_0^t K\mathrm{d}t \tag{A4}$$

The left hand side infinite integral has the following solution:

$$-2\int_{\beta} \frac{d\beta}{(b^2-\beta^2)\beta^2} = \frac{2}{b^2}\frac{1}{\beta} + \frac{1}{b^3}\ln\frac{b-\beta}{b+\beta} \tag{A5}$$

since:

$$\frac{2}{(b-\beta^2)\beta^2} = \frac{2}{b^2}\frac{1}{\beta^2} + \frac{1}{b^3}\left(\frac{1}{b-\beta} + \frac{1}{b+\beta}\right)$$

Integrating Eq. (A5) from $\beta_0 = 1$ to β gives:

$$g(\beta) = \frac{2}{b^2}\left(\frac{1}{\beta} - 1\right) + \frac{1}{b^3}\ln\frac{b-\beta}{b+\beta}\frac{b+1}{b-1} = Kt \qquad \text{(A6)}$$

where: $\beta = (1-\alpha)^{1/2}$; and $b = (B+1)^{1/2}$.

The integral solution of $g(\alpha)$ for $n = 1$ is similar to Eq. (A3), viz.

$$g(\alpha) = \frac{1}{1+B}\ln\frac{B+\alpha}{B(1-\alpha)} = Kt \qquad \text{(A7)}$$

while that of $g(\beta)$ for $n = 1/2$ is similar to Eq. (A6):

$$g(\beta) = \frac{1}{b}\ln\frac{b-\beta}{b+\beta}\frac{b+1}{b-1} = Kt \qquad \text{(A8)}$$

where: the variable β and the parameter b have the same meaning as those in Eq. (A6), i.e.: $\beta = (1-\alpha)^{1/2}$ and $b = (B+1)^{1/2}$.

Appendix B. Derivation of the velocity equation of the partially reacted samples.

The change of the variable is based on the energy balance, viz.

$$\alpha - \alpha_0 = \frac{\Delta H}{\Delta H_t} = \frac{\Delta H}{\Delta H_r}\frac{\Delta H_t - \Delta H_i}{\Delta H_t} = \alpha'(1-\alpha_0)$$

where: ΔH_i and ΔH_r are the initial and residual enthalpy of partially reacted epoxy–amine system; ΔH and ΔH_t are the current and ultimate enthalpy of the reaction; α_0 is the initial degree of conversion.

Then, replacing the variable $\alpha' = (\alpha - \alpha_0)/(1-\alpha_0)$ into Eq. (3), one can obtain:

$$\frac{d\alpha'}{dt} = \frac{d\alpha'}{dT}\frac{dT}{dt} = K'_0\exp(-E_a/RT)(B+\alpha')(1-\alpha')^n$$

where: $K'_0 = K_0(1-\alpha_0)^n$ and $B' = (B+\alpha_0)/(1-\alpha_0)$.

References

[1] Horie K, Hiura H, Sawada M, Mita I, Kambe H. J Polym Sci 1970;A8:1357.
[2] Smith IT. Polymer 1961;2:95.
[3] Rozenberg AA. Adv Polym Sci 1985;75:113.
[4] Dusek K. Adv Polym Sci 1985;78:1.
[5] Riccardi CC, Williams RJJ. Polymer 1986;27:913.
[6] Chiao L. Macromolecules 1990;23:1286.
[7] Cole KC. Macromolecules 1991;24:3093.
[8] Mijovic J, Fishbain A, Wijaya J. Macromolecules 1992;25:979.
[9] Xu L, Fu JH, Schlup JR. J Am Chem Soc 1994;116:2821.
[10] Sourour S, Kamal MR. Thermochim Acta 1976;14:41.
[11] Enns JB, Gillham JK. J Appl Polym Sci 1983;28:2567.
[12] Wisanrakkit G, Gillham JK, Enns JB. J Appl Polym Sci 1990;41:1895.
[13] Riccardi CC, Adabbo HE, Williams RJJ. J Appl Polym Sci 1984;29:2481.
[14] Huguenin FGAE, Klein MT. IEC Prod Res Dev 1985;24:166.
[15] Urbaczewski E, Pascault JP, Sautereau H, Riccardi CC, Moschiar SM, Williams RJJ. Macromol Chem 1990;191:943.
[16] Wisanrakkit G, Gillham JK. J Appl Polym Sci 1990;41:2885.
[17] Verchere D, Sautereau H, Pascault JP, Riccardi CC, Moschiar SM, Williams RJJ. Macromolecules 1990;23:725.
[18] Bajaj P, Jha NK, Kumar RA. J Appl Polym Sci 1990;40:203.
[19] Moschiar SM, Riccardi CC, Williams RJJ, Verchere D, Sautereau H, Pascault JP. J Appl Polym Sci 1991;42:717.
[20] Deng Y, Martin GC. Macromolecules 1994;27:5147.
[21] Girard-Reydet E, Riccardi CC, Sautereau H, Pascault JP. Macromolecules 1995;28:7599.
[22] Kamal MR, Sourour S, Ryan ME. SPE Tech Pap 1973;19:187.
[23] Ryan ME, Dutta A. Polymer 1979;20:203.
[24] Dutta A, Ryan ME. J Appl Polym Sci 1979;24:635.
[25] Flammersheim HJ, Horhold HH, Bellstedt K, Klee J. Makromol Chem 1983;184:113.
[26] Spacek V, Pouchly J, Biros J. Eur Polym J 1987;23:377.
[27] Abuin SP, Pellin MP, Nunes L. J Appl Polym Sci 1990;41:2155.
[28] Min BG, Stachurski ZH, Hodgkin JH. Polymer 1993;34:4488.
[29] Scott EP, Zoubier S. Polym Eng Sci 1993;34:1165.
[30] Wise CW, Cook WD, Goodwin AA. Polymer 1997;38:3251.
[31] Abuin SP, Pellin MP, Pazos MP, Lopez-Quentela L. Polymer 1997;38:3795.
[32] Barton JM. Makromol Chem 1973;171:247.
[33] Barton JM. J Macromol Sci—Chem 1974;A8:25.
[34] Barton JM. Adv Polym Sci 1985;72:111.
[35] Galy J, Sabra A, Pascault JP. Polym Eng Sci 1986;26:1514.
[36] Prime RB. In: Porter RS, Johnson JF, editors. Analytical calorimetry, vol. 2. New York: Plenum Press, 1970. p. 201.
[37] Prime RB. Polym Eng Sci 1973;13:365.
[38] Stark EB, Seferis JC, Apicella A, Nicolais L. Thermochim Acta 1984;77:19.
[39] Ninan KN, Krishnan K. Thermochim Acta 1985;92:185.
[40] Vyazovkin S, Sbirrazzuoli N. Macromolecules 1996;29:1867.
[41] Wisanrakkit G, Gillham JK. J Appl Polym Sci 1991;42:2453.
[42] Dutta A, Ryan ME. Thermochim Acta 1979;33:87.
[43] Zvetkov VL. In: Mechanics and Technology of Composite Materials, Proc VIII Int Conf, Sofia, 1997. p. 408.
[44] Friedmann HL. J Polym Sci 1966;C6:917.
[45] Ozawa T. Bull Chem Soc Japan 1966;38:1881.
[46] Doyle CD. J Appl Polym Sci 1961;5:285.
[47] Doyle CD. Nature 1965;207:290.
[48] Brown WE, Dollimore D, Galway AK. Reactions in solid state. In: Bamford CH, Tipper CFH, editors. Comprehensive chemical kinetics, vol. 22. Amsterdam: Elsevier, 1980. p. 103.
[49] Borchardt HJ, Daniels F. J Am Chem Soc 1957;79:41.
[50] Grey AP. In: Porter RS, Johnson JF, editors. Analytical calorimetry, vol. 1. New York: Plenum Press, 1968.
[51] Coates AW, Redfern JP. Nature 1964;201:68.
[52] Zvetkov VL. The next paper of the present series.